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In re Japanese Application of

Koji UTSUGI, et al.

Japanese Patent Application No.: 2003-416516

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for: "Electrolyte solution for secondary battery and secondary battery using the same"

VERIFICATION OF TRANSLATION

Honorable Commissioner of Patents and Trademarks

Washington, D.C. 20231

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- (2) that he translated the above-identified Japanese Application from Japanese to English;
- (3) that the attached English translation is a true and correct translation of the above-identified Japanese Application to the best of his knowledge and belief; and
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Akinori OHTA

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[TITLE OF THE INVENTION] ELECTROLYTE SOLUTION FOR SECONDARY BATTERY AND SECONDARY BATTERY USING THE SAME

[TECHNICAL FIELD]

5 [0001]

The present invention relates to an electrolyte solution for secondary battery and a secondary battery using the same.

[BACKGROUND OF THE INVENTION]

[0002]

10 A non-aqueous electrolyte solution type lithium-ion or lithium secondary battery in which a carbon material, oxide, lithium alloy or lithium metal is used in an anode while a lithium-containing transition metal complex oxide is used in a cathode has drawn attention as an electric source for a cellular phone, a notebook computer or the like because it can realize a higher energy density. It is generally known that in such a secondary battery, a film which is
15 called a surface film, a protective film, an SEI or a membrane is formed on an electrode surface. It is also well-known that controlling the surface film is essential for improving electrode performance because the surface film significantly influences a charge/discharge efficiency, a cycle life and safety. Specifically, when using a carbon material or an oxide material as an anode material, its irreversible capacity must be reduced, and in a lithium-metal anode or
20 lithium alloy anode, a charge/discharge efficiency must be reduced while a safety problem due to dendrite formation must be solved.

[0003]

There have been suggested a variety of procedures for solving the problems. For example, there has been suggested that a membrane layer made of, e. g., lithium fluoride is
25 formed on a surface of lithium metal or lithium alloy by a chemical reaction to suppress formation of dendrites.

[0004]

Patent document 1 has disclosed that a lithium anode is exposed to an electrolyte solution containing hydrofluoric acid for initiating a reaction of the anode with hydrofluoric acid
30 to coat the surface of the anode with a lithium fluoride film. Hydrofluoric acid is generated by a reaction of LiPF₆ with a small amount of water. On the other hand, a surface film of lithium hydroxide or lithium oxide is formed on the surface of the lithium anode by autoxidation in the air. These react to form a surface film of lithium fluoride on the anode surface. However, since the lithium fluoride film is formed by utilizing a reaction of an electrode interface with a

liquid, the surface film may tend to be contaminated with byproducts, leading to an uneven film. Sometimes, a surface film of lithium hydroxide or lithium oxide may not be formed as an even film or in some area lithium may be exposed. Such cases may lead to not only an uneven film, but also a safety problem due to a reaction of lithium with water or hydrogen fluoride and so on.

- 5 An insufficient reaction may lead to a residue of undesired compounds other than fluoride, which may be harmful by causing reduction in ion conductivity. Furthermore, in a process for forming a fluoride layer utilizing a chemical reaction in such an interface, there are limitations to fluorides or electrolyte solutions which can be used. It may be, therefore, difficult to form a stable surface film in a good yield.

10 [0005]

In patent document 2, a mixed gas of argon and hydrogen fluoride is reacted with an aluminum-lithium alloy to form a surface film of lithium fluoride on an anode surface. However, if a preformed surface film is present on the surface of lithium metal, in particular if a plurality of components are present, the reaction tends to be uneven, which may make it
15 difficult to form an even lithium fluoride film. In such a case, it is difficult to obtain a lithium secondary battery exhibiting satisfactory cycle properties.

[0006]

Patent document 3 has disclosed that a surface membrane structure comprising a material with a rock-salt type crystal structure as a main component is formed on surface of a
20 lithium sheet in which an even crystal structure, i. e., a (100) crystal face, is preferentially oriented. It has been thus described that an even precipitation/dissolution reaction, i. e., an even battery charge/discharge can be achieved, resulting in prevention of dendrite precipitation of lithium metal and improvement in a battery cycle life. A material used in a surface film preferably comprises a lithium halide, which is preferably comprised of solid solution of at least
25 one selected from the group consisting of LiCl, LiBr and LiI with LiF. Specifically, for forming a solid solution membrane of at least one selected from the group consisting of LiCl, LiBr and LiI with LiF, a lithium sheet formed by pressing (rolling) in which a (100) crystal face is preferentially oriented is immersed in an electrolyte solution containing at least one among chlorine molecules or chloride ions, bromine molecules or bromide ions, and iodine molecules or
30 iodide ions and containing fluorine molecules or fluoride ions to form an anode for a non-aqueous electrolyte battery. In this technique, an rolled lithium metal sheet is used. Since the lithium sheet tends to be exposed in the air, a membrane derived from moisture and so on may be formed on its surface, leading to uneven distribution of active sites. It may be, therefore, difficult to form a desired stable surface film. Thus, this technique has not always

been effective for adequately preventing dendrite formation.

[0007]

There has been described a technique that a capacity and a charge/discharge efficiency can be improved when using as an anode a carbon material such as graphite and hard carbon in
5 which lithium ions can be occluded and released.

[0008]

Patent document 4 has suggested an anode where a carbon material is coated with aluminum, whereby reductive decomposition of a solvent molecule in a solvate with a lithium ion on the carbon surface is reduced to suppress reduction in a cycle life. However, since
10 aluminum reacts with a small of moisture, repeated cycles may lead to rapid reduction in a capacity.

[0009]

Patent document 5 has suggested an anode in which a carbon material surface is coated with a film of a lithium-ion conductive solid electrolyte, whereby decomposition of a
15 solvent when using a carbon material can be suppressed, so that a lithium ion secondary battery which particularly allows propylene carbonate to be used can be provided. However, change of stress during insertion and removal of lithium ions generates cracks in the solid electrolyte, which may lead to deteriorated properties. Due to unevenness such as crystal defects in the solid electrolyte, an even reaction cannot be achieved in the anode surface,
20 sometimes leading to a reduced cycle life.

[0010]

Patent document 6 has disclosed a secondary battery wherein an anode is made of a graphite-containing material and an electrolyte solution comprises a cyclic and linear carbonates as a main component and 0.1 weight% to 4 weight% both inclusive of
25 1,3-propanesultone and/or 1,4-butanesultone as a cyclic monosulfonate. It is believed that 1,3-propanesultone or 1,4-butanesultone contributes to formation of a passive membrane on a carbon material surface, which can coat an active and highly crystallized carbon material such as natural or artificial graphite with the passive membrane to prevent decomposition of an electrolyte solution without deterioration of a normal reaction in a battery. Patent documents
30 7 and 8 have described that in addition to a cyclic disulfonate, a linear disulfonate may be similarly effective. However, using the cyclic sulfonate in patent document 6 or the linear disulfonates in Patent documents 7 and 8, a membrane may be formed mainly on an anode while forming a membrane on, for example, a cathode may be substantially difficult.

[0011]

Patent document 9, an aromatic compound is added to a solvent for an electrolyte solution for preventing oxidation of the solvent for an electrolyte solution to suppress deterioration in a capacity after long-term repetition of charge/discharge of a secondary battery. This is a technique for preventing solvent decomposition by preferentially decomposing the 5 aromatic compound by oxidation. However, when using the additive, a cathode surface is not coated, resulting in insufficient improvement in cycle properties. Patent document 10 has described that a nitrogen-containing unsaturated cyclic compound is added to an electrolyte solution to improve cycle properties when using a high-voltage cathode. However, while the nitrogen-containing unsaturated cyclic compound can improve a charge/discharge efficiency in 10 an anode, it cannot improve a charge/discharge efficiency in a cathode.

[0012]

On the other hand, non-patent documents 1 and 2 disclose methods for manufacturing a disulfonate compound. In patent document 11, there is described that a disulfonate compound is obtained as a byproduct of a cyclic disulfonate synthesis.

15 [Patent document 1] JPhei7-302617

[Patent document 2] JPhei8-250108

[Patent document 3] JPhei11-288706

[Patent document 4] JPhei5-234583

[Patent document 5] JPhei5-275077

20 [Patent document 6] JP2000-3724

[Patent document 7] JP2000-133304

[Patent document 8] US-6436582B1

[Patent document 9] JP2003-7334

[Patent document 10] JP2003-115324

25 [Non-patent document 1] J. Am. Pham. Assoc., Vol.126, pp.485-493 (1937)

[Non-patent document 2] G. Schroeter, Lieb, Ann, Der Chemie, Vol.418, pp.161-257 (1919)

[Patent document 11] JPhei5-44946

[DISCLOSURE OF THE INVENTION]

[TECHNICAL PROBLEM TO BE SOLVED BY THE INVENTION]

30 [0013]

The related art had the following problems in common.

Although the surface films generated on the surfaces of the electrodes have deep influence on charge/discharge efficiency, cycle life and safety depending on their properties, there has been no technique to enable control of the film over a long period of time. For

example, although if the surface film made of lithium halide or glassy oxide is formed on the film made of lithium or an alloy thereof, an effect of suppressing dendrite could be obtained to a certain extent at the initial use, when it was used repeatedly, the surface film might be impaired to deteriorate the function as a protection film. This is considered to be attributable
 5 to the fact that the occlusion and release of lithium cause changes in volume of the layer made of lithium or lithium alloy while the film formed on the surface thereof and made of lithium halide and so on scarcely changes in volume and therefore, internal stress occurs within these layers and the interfaces therebetween. When such internal stress occurs, in particular, the surface film made of lithium halide and so on is partly damaged, which is supposed to cause
 10 deterioration of dendrite suppressing function.

[0014]

When carbon materials such as graphite were used for anode, there were cases where electric charge resulted from decomposition of the solvent molecules or anions appeared as an irreversible capacity component, and caused decrease in the initial charge/discharge efficiency.
 15 The composition, crystal state, stability, etc. of the film resulted at this stage may significantly adversely affect the subsequent efficiency and the cycle life.

As for a secondary battery having a high voltage of 4.5 V or more and using a lithium-containing transition metal complex oxide as cathode, the decomposition of the solvent molecules may occur on the cathode, resulting in the reduction of the cycle life. As mentioned
 20 above, researches have been conducted aiming at improving charge/discharge efficiency, cycle life and so on by forming a membrane on the electrode for a secondary battery. However, generally, sufficient battery characteristics have not been achieved yet.

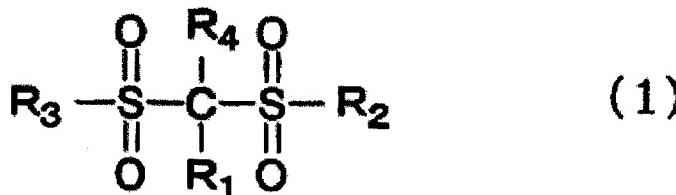
[MEANS FOR SOLVING PROBLEM]

[0015]

25 In order to solve the problems, the present invention has the following construction. That is, the present invention is an electrolyte solution for secondary battery comprising an aprotic solvent and at least a compound represented by the following general formula (1):

[0016]

[formula 2]



wherein R₁ and R₄ independently represent a hydrogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted alkoxy group, or a halogen atom; and R₂ and R₃ independently represent a substituted or unsubstituted alkyl group, a substituted or unsubstituted phenoxy group, a substituted or unsubstituted alkoxy group, a hydroxyl group, a halogen atom, or a substituted or unsubstituted amino group.

5 [0017]

It is preferable that the electrolyte solution for secondary battery of the present invention further comprises a lithium salt as an electrolyte salt.

10 It is preferable that the electrolyte solution for secondary battery of the present invention further comprises at least one selected from the group consisting of 1,3-propane sultone, 1,4-butane sultone, sulfolane, alkane sulfonic anhydride, cyclic disulfonate compound, γ -sultone compound and sulfolene compound.

It is preferable that the electrolyte solution for secondary battery of the present invention further comprises at least one of vinylene carbonate and the derivatives thereof.

15 [0018]

It is preferable that in the electrolyte solution for secondary battery of the present invention, further, the aprotic solvent is at least one organic solvent selected from the group consisting of cyclic carbonates, linear carbonates, aliphatic carboxylates, γ -lactones, cyclic ethers, linear ethers and fluoride derivatives thereof.

20 It is preferable that in the electrolyte solution for secondary battery of the present invention, further, the lithium salt is at least one lithium salt selected from the group consisting of LiPF₆, LiBF₄, LiAsF₆, LiSbF₆, LiClO₄, LiAlCl₄, LiN(C_kF_{2k+1}SO₂)₂ and LiN(C_kF_{2k+1}SO₂)(C_mF_{2m+1}SO₂), wherein k and m are independently 1 or 2.

[0019]

25 The present invention relates to a secondary battery having a cathode, an anode and an electrolyte solution for secondary battery characterized in that the electrolyte solution for secondary battery is said electrolyte solution for secondary battery.

It is preferable that in the secondary battery of the present invention, further, the cathode includes a lithium-containing complex oxide which can occlude and release lithium.

30 It is preferable that in the secondary battery of the present invention, further, the anode includes a metal material which can form an alloy with lithium metal or lithium as a anode active material which can occlude and release lithium.

It is preferable that in the secondary battery of the present invention, further, the anode includes carbon as an anode active material.

It is preferable that in the secondary battery of the present invention, further, the carbon is graphite.

It is preferable that in the secondary battery of the present invention, further, the carbon is amorphous carbon.

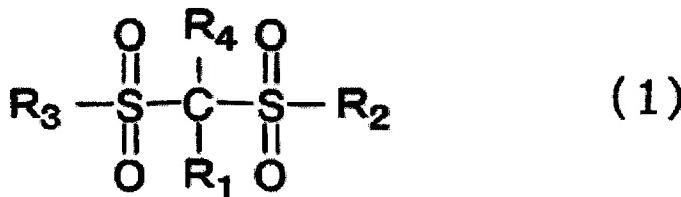
5 [EFFECTS OF THE INVENTION]

[0020]

According to the present invention, by using an electrolyte solution for secondary battery which contains a disulfonate compound represented by the general formula (1) in an aprotic solvent, or an electrolyte solution for secondary battery which further contains a sulfonate compound other than the above disulfonate compound or vinylene carbonate in this electrolyte solution, a lithium secondary battery having properties such as excellent energy density and electromotance and having excellent cycle life and safety can be obtained.

[0021]

[formula 3]



15

wherein R₁ and R₄ independently represent a hydrogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted alkoxy group, or a halogen atom; and R₂ and R₃ independently represent a substituted or unsubstituted alkyl group, a substituted or unsubstituted phenoxy group, a substituted or unsubstituted alkoxy group, a hydroxyl group, a halogen atom, or a substituted or unsubstituted amino group.

[BEST MODE FOR CARRYING OUT THE INVENTION]

[0022]

Figure 1 shows an outlined structure of one exemplary of a battery according to the present invention, which is composed of a cathode current collector 11; a layer 12 comprising a cathode active material made of any one of oxide or sulfuric compound, electro conductive polymer and stabilized radical compound, or mixture thereof which can occlude and release lithium ions; a layer 13 comprising an anode active material made of any one of carbon material or oxide, metal for forming alloy with lithium, and lithium metal itself, or mixture thereof which occlude and release lithium ions; an anode current collector 14; an electrolyte solution 15; and a porous separator 16 including the electrolyte solution. Here, the vinyl disulfonate

compound represented by the general formula (1) is contained in the electrolyte solution 15 which includes lithium salt as an electrolyte.

[0023]

As the cathode current collector, aluminum, stainless steel, nickel, titanium or an alloy 5 thereof and so on can be used, and as the anode current collector, copper, stainless steel, nickel, titanium or an alloy thereof can be used.

[0024]

As an aprotic solvent, one or two or more thereof as a mixture of the following aprotic solvent may be used:

10 Cyclic carbonates such as propylene carbonate (hereinafter abbreviated as PC), ethylene carbonate (hereinafter abbreviated as EC), butylene carbonate (BC) and vinylene carbonate (VC);

Linear carbonates such as dimethyl carbonate (DMC), diethyl carbonate (hereinafter abbreviated as DEC), ethyl methyl carbonate (EMC), dipropyl carbonate (DPC);

15 Aliphatic carboxylates such as methyl formate, methyl acetate, ethyl propionate; γ -lactones such as γ -butyrolactone;

Linear ether such as 1,2-ethoxyethane (DEE), ethoxymethoxyethane (EME);

Cyclic ethers such as tetrahydrofuran, 2-methyltetrahydrofuran;

20 Aprotic organic solvent such as dimethylsulfoxide, 1,3-dioxolan, formamide, acetamide, dimethylformamide, dioxolan, acetonitrile, propionitrile, nitromethane, ethylmonoglyme, phosphotriester, trimethoxymethane, dioxolan derivatives, sulfolane, methylsulfolane, 1,3-dimethyl-2-imidazolidinone, 3-methyl-2-oxazolidinone, propylene carbonate derivatives, tetrahydrofuran derivatives, ethylether, 1,3-propane sultone, anisole, N-methylpyrrolidone, fluoride carboxylate ester.

25 [0025]

By adding or mixing at least one of vinylene carbonate and the derivatives thereof in the electrolyte solution, an improvement of the cycle properties can be further achieved. One or a combination of a plurality of materials among these materials can be used. When the vinylene carbonate or the derivatives thereof is used as an additive, the effect thereof can be 30 obtained by the addition of 0.01 weight% to 10 weight% to the electrolyte solution. Moreover, when the vinylene carbonate or the derivatives thereof is used as a solvent of liquid, the effect thereof can be obtained by the addition of 1 weight% to 5 weight% to the liquid.

[0026]

The electrolyte solution may contain the lithium salt. The lithium salt is preferably

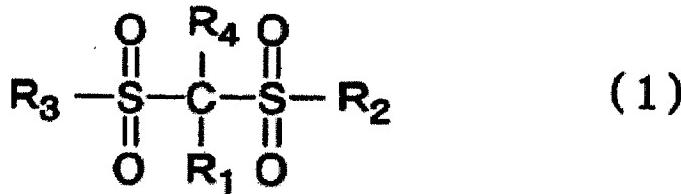
at least one selected from the group consisting of LiPF₆, LiBF₄, LiAsF₆, LiSbF₆, LiClO₄, LiAlCl₄, LiN(C_kF_{2k+1}SO₂)₂ and LiN(C_kF_{2k+1}SO₂) (C_mF_{2m+1}SO₂), wherein k and m are independently 1 or 2. Among these, LiPF₆ and LiBF₄ are preferable. High energy density can be attained when such a lithium salt is contained.

5 [0027]

The electrolyte solution according to the present invention is characterized in that it comprise a compound represented by the following general formula (1):

[0028]

[formula 4]



10

wherein R₁ and R₄ independently represent a hydrogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted alkoxy group, or a halogen atom; and R₂ and R₃ independently represent a substituted or unsubstituted alkyl group, a substituted or unsubstituted phenoxy group, a substituted or unsubstituted alkoxy group, a hydroxyl group, a 15 halogen atom, or a substituted or unsubstituted amino group.

When R₁ to R₄ are an alkyl group or alkoxy group, their carbon atom number is preferably 1 to 4. By making their carbon atom number become 1 to 4, it is possible to provide the lithium secondary battery which has excellent cycle life and safety. When R₁ to R₄ are an 20 substituted alkyl group or substituted alkoxy group, a halogen atom or hydroxyl group may be used as a substituted group. By make the substituted group become the halogen atom or hydroxyl group, it is possible to provide the stably usable secondary battery which has an improved electromotance.

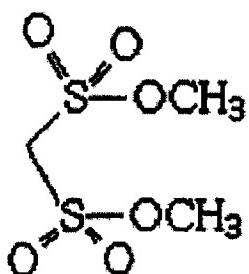
[0029]

Specific examples of compound represented by the general formula (1) are shown below, 25 but the present invention is not limited to these.

[0030]

[formula 5]

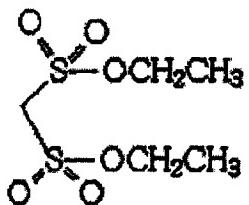
Compound No.1



[0031]

[formula 6]

Compound No.2

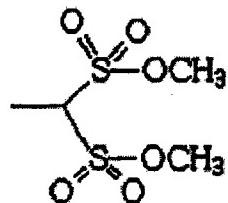


5

[0032]

[formula 7]

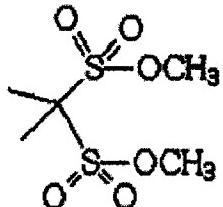
Compound No.3



10 [0033]

[formula 8]

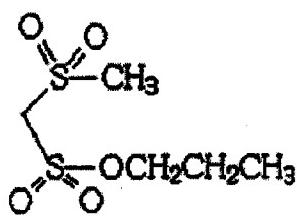
Compound No.4



[0034]

15 [formula 9]

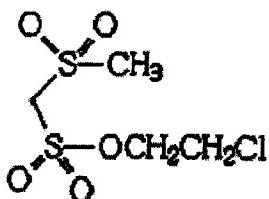
Compound No.5



[0035]

[formula 10]

Compound No.6

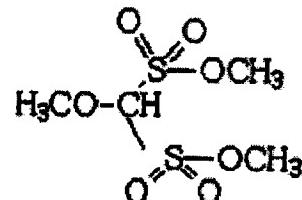


5

[0036]

[formula 11]

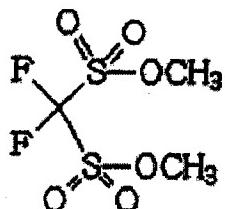
Compound No.7



10 [0037]

[formula 12]

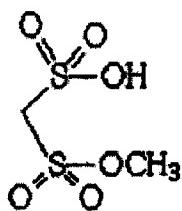
Compound No.8



[0038]

15 [formula 13]

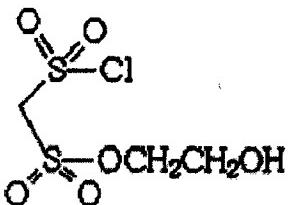
Compound No.9



[0039]

[formula 14]

Compound No.10

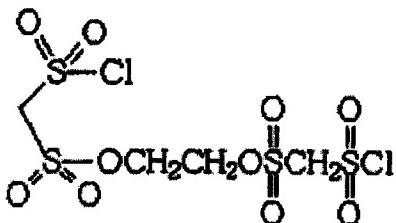


5

[0040]

[formula 15]

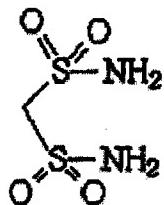
Compound No.11



10 [0041]

[formula 16]

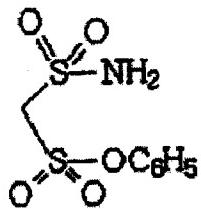
Compound No.12



[0042]

15 [formula 5]

Compound No.13



By containing these materials in the electrolyte solution, it is possible to provide the secondary battery which has more excellent energy density and electromotance. The compounds represented by the general formula (1) can be manufactured by for example, 5 methods described in non-patent documents 1 and 2, and patent document 11.

[0043]

The compound represented by the general formula (1) is preferably contained in an amount of 0.01 weight% to 10 weight % in the electrolyte solution. The effect is not be sufficiently exhibited below 0.1 weight % in the membrane formation on the surface of the 10 electrodes. Since if it exceeds 10 weight %, the compound is not dissolved and at the same time the viscosity of the electrolyte solution increases, therefore, its weight% is not preferable. More preferably, the compound is added in a range of 0.1 weight % to 5 weight % in the present invention, which results in more sufficient film coating effect.

[0044]

15 Preferably, the electrolyte solution further includes at least one selected from the group consisting of 1,3-propane sultone, 1,4-butane sultone, sulfolane, alkane sulfonic anhydride, cyclic disulfonate compound, γ -sultone compound and sulfolene compound. It is considered that these materials contribute to the formation of passivation film on the surface of anode and have effects for suppressing a decomposition of the electrolyte solution without 20 deteriorating a normal reaction of battery by coating the surface of anode with the passivation film. The content of these materials in the electrolyte solution is preferably in a range of 0.1 weight % to 4 weight %.

[0045]

25 The anode active material is composed of lithium metal, lithium alloy or a material such as a carbon material or oxide which can occlude and release lithium.

As the carbon material, graphite, amorphous carbon, diamond-like carbon, carbon nanotube, carbon nanohorn, etc. or a composite material thereof occluding lithium may be used.

[0046]

30 As the oxide, any one of silicon oxide, tin oxide, indium oxide, zinc oxide, lithium oxide, phosphoric acid and boracic acid, or compound thereof may be used. In particular, silicon oxide

is preferably contained. The structure of silicon oxide is preferably amorphous condition. This is because that the silicon oxide is stable and does not react with the other compound, and further the amorphous structure does not induce the deterioration due to ununiformity such as the crystal grain boundary and crystal defect. As film forming method for a layer including the anode active material, a vapor deposition method, a CVD method, or a sputtering method and so on may be used.

[0047]

The lithium alloy is composed of lithium and metal which can form alloy with lithium. For example, the lithium alloy is composed of a binary or ternary alloy, or an alloy of four or 10 more types of metals which comprises metal such as Al, Si, Pb, Sn, In, Bi, Ag, Ba, Ca, Hg, Pd, Pt, Te, Zn and La and lithium. As the lithium metal and lithium alloy, particularly, amorphous-like alloy is preferable. This is because that the amorphous structure is hard to induce the deterioration due to ununiformity such as the crystal grain boundary and crystal defect.

15 [0048]

The lithium metal or lithium alloy may be formed by an appropriate method such as a melt cooling method, a liquid rapid cooling method, an atomization method, a vacuum vapor deposition method, a sputtering method, a plasma CVD method, a photo CVD method, a thermal CVD and a sol-gel method. By using these materials as the anode active material, it 20 is possible to provide the secondary battery which has higher energy density.

[0049]

In the present invention, it is possible to use a complex oxide which is Li_bZO_2 , wherein Z is at least one transition metal, for example, Li_bCoO_2 , Li_bNiO_2 , $\text{Li}_b\text{Mn}_2\text{O}_4$, Li_bMnO_3 , $\text{Li}_{b-d}\text{Cr}_{1-d}\text{O}_2$ ($0 < b < 1$, $0 < d < 1$), or an organic sulfuric compound, an electro conductive polymer, 25 an organic radical compound, as the cathode active material. Moreover, it is possible to use a lithium-containing complex oxide having a plateau at 4.5V or more as potential with reference to lithium metal. The lithium-containing complex oxide includes a spinel-type lithium-manganese complex oxide, olivine-type lithium-containing complex oxide, an inverse spinel-type lithium-containing complex oxide and so on. For example, the lithium-containing 30 complex oxide may be the compound represented by the general formula, $\text{Li}_a(\text{A}_x\text{Mn}_{2-x})\text{O}_4$, wherein x is $0 < x < 2$ and a is $0 < a < 1.2$, and A is at least one selected from the group consisting of Ni, Co, Fe, Ti, Cr and Cu. By using these materials as the cathode active material, it is possible to provide the secondary battery which has higher energy density.

[0050]

The cathode according to the present invention can be obtained by a method of distributing and mixing these active materials with a conductive material such as carbon black and a binder such as polyvinylidene fluoride (PVDF) in a solvent such as N-methyl-2-pyrrolidone (NMP), and applying the resulting material on the substrate such as an aluminum foil.

[0051]

The lithium secondary battery according to the present invention can be manufactured by laminating an anode and a cathode with a separator therebetween or rolling such a laminate in a dry air or inactive gas atmosphere, and then setting the resulting structure in the battery can or sealing the resulting structure using a flexible film and so on made of laminated body a synthetic resin and metallic foil. As the separator, a porous film such as polyolefin such as polypropylene and polyethylene and a fluororesin is used.

[0052]

The shape of the secondary battery according to the present invention is particularly not limited, and includes a cylindrical-type, a square-type, a coin-type and a laminate-type.

[EXAMPLES]

[0053]

(Example 1)

(Fabrication of battery)

An aluminum foil having a thickness of 20 μm was used as cathode current collector 11, and LiMn₂O₄ was used as cathode active material in the cathode 12. Vapor-deposited lithium metal having a thickness of 20 μm was used as anode 13 on copper foil of anode current collector 14 having a thickness of 10 μm . The mixed solvent (volume ratio: 30/70) of EC and DEC was used as solvent of the electrolyte solution 15. LiPF₆ of 1 mol/L was dissolved in this solvent. The compound No. 1 of 0.5 weight% was added and dissolved in this solvent as an additive. Coin-type secondary battery was fabricated by laminating the anode and cathode with the separator 16 which consists of polyethylene therebetween.

[0054]

(Charge/discharge cycle test)

The charge rate, the discharge rate, the charge termination voltage, the discharge termination voltage and the utilization ratio (discharge depth) of lithium metal anode were adjusted to 0.05C, 0.1C, 4.2V, 3.0V and 33% respectively at temperature of 20°C. The capacity retention ratio (%) is a value obtained by dividing a discharge capacity (mAh) after 100 cycles by a discharge capacity (mAh) of the tenth cycle. The following table 1 shows the result

obtained by the cycle test.

[0055]

(Example 2)

The battery was fabricated using the compound No.3 instead of additive represented in
5 example 1. The battery was fabricated and evaluated as example 1 except that. Table 1
shows the result of cycle properties as example 1.

[0056]

(Comparative Example 1)

The battery as example 1 was fabricated and the cycle properties was evaluated as
10 example 1 except that the compound represented by the formula (1) was not added in the
electrolyte solution. Table 1 shows the result.

[0057]

The capacity retention ratios of examples 1 and 2 exceed that of comparative example
1 greatly. It is conceivable that this is because the surface film at interface between the anode
15 surface and the electrolyte was stabilized and an irreversible reaction was suppressed due to its
higher ion conductivity.

[0058]

[Table 1]

	Example 1	Example 2	Comparative Example 1
Anode Active Material	Li metal	Li metal	Li metal
Additive	Compound No. 1	Compound No. 3	None
Capacity retention ratio (%) at 100 cycle	87.6	86.8	45.7

(Example 3)

20 The battery as example 1 was fabricated and the cycle properties (the cycle properties
was measured up to 300 cycles.) was evaluated as example 1 except that the anode active
material was composed of graphite material. Table 2 shows the result thereof. As for the
battery shown in the present example, the anode surface after cycle test was investigated with
X-ray photoelectron spectroscopy (XPS) and energy dispersive X-ray analysis (EDX), which
25 revealed the existence of LiF and LiCO₃. Furthermore, as a result of performing peak division
of the sulfur spectrum by XPS analysis, it was confirmed that the substance having a peak near
164 eV existed. Since there was no substance having a peak near 164 eV in the systems using
no additive and using the other additive, it is conceivable that the membrane peculiar to the

disulfonate compound of the present invention had been formed.

[0059]

(Example 4)

The battery as example 1 was fabricated and the cycle properties (the cycle properties
5 was measured up to 300 cycles.) was evaluated as example 1 except that the mixed solvent
(volume ratio: 20/20/60) of PC, EC and DEC was used as the electrolyte solvent instead of the
mixed solvent (volume ratio: 30/70) of EC and DEC, and amorphous carbon was used as anode
active material. Table 2 shows the result thereof. As for the battery shown in the present
example, the anode surface after cycle test was investigated with X-ray photoelectron
10 spectroscopy (XPS) and energy dispersive X-ray analysis (EDX), which revealed the existence of
LiF and LiCO₃. Furthermore, as a result of performing peak division of the sulfur spectrum by
XPS analysis, it was confirmed that the substance having a peak near 164 eV existed. Since
there was no substance having a peak near 164 eV in the systems using no additive and using
the other additive, it is conceivable that the membrane peculiar to the disulfonate compound of
15 the present invention had been formed.

[0060]

(Comparative Example 2)

The battery of comparative example 3 was fabricated as example 3 except that the
additive was not added. As for this battery, the evaluation as example 1 was performed.

20 [0061]

(Comparative Example 3)

The battery of comparative example 3 was fabricated as example 4 except that the
additive was not added. As for this battery, the evaluation as example 1 was performed.

Table 2 shows the result of examples 3 and 4 and comparative examples 2 and 3. It is
25 confirmed that examples using the compound represented by the general formula (1) as
additive have the higher capacity retention ratios during cycle tests with reference to
comparative examples. According to this result, if any one of graphite and amorphous carbon
was used as anode active material, the effects as example 1 appeared.

[0062]

30 [Table 2]

	Example 3	Example 4	Comparative Example 2	Comparative Example 3
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Anode Active Material	Graphite	Amorphous carbon	Graphite	Amorphous carbon
Additive	Compound No. 1	Compound No. 1	None	None
Electrolyte solvent	EC/DEC	PC/EC/DEC	EC/DEC	PC/EC/DEC
Capacity retention ratio (%) at 300 cycle	89.8	88.1	81.8	79.9

(Example 5)

(Fabrication of battery)

- Fabrication of battery of the present example will be explained. An aluminum foil having a thickness of 20 µm was used as cathode current collector, and LiMn₂O₄ was used as cathode active material in the cathode. Vapor-deposited lithium metal having a thickness of 20 µm was used as anode active material on copper foil of anode current collector having a thickness of 10 µm. The mixed solvent (volume ratio: 30/70) of EC and DEC was used as solvent of the electrolyte solution. LiPF₆ of 1 mol/L was dissolved as support electrolyte. The compound No. 1 of 0.5 weight% was used in the electrolyte solution as an additive. Further, 1,3-propanesultone (hereinafter abbreviated as 1,3-PS) of 1 weight% was contained in the electrolyte solution, and the electrolyte solution of the present example 6 was manufactured.

The secondary battery was fabricated by laminating anode and cathode with the separator which consists of polyethylene therebetween.

[0063]

- 15 (Charge/discharge cycle test)

The measurement was performed as the method described in example 1. Table 3 shows the result obtained.

[0064]

(Example 6)

- 20 The battery was fabricated and evaluated as example 4 except that 1,3-PS of 1 weight% was added to the electrolyte solution of example 4. Table 3 shows the result of cycle properties as example 4

[0065]

- 25 The capacity retention ratios of examples 5 and 6 after cycle tests exceed that of example 1 or 4 respectively. It is conceivable that this is because the addition of 1,3-PS stabilized membrane at interface between the electrode surface and the electrolyte and an irreversible reaction was suppressed due to higher ion conductivity of the film.

[0066]

[Table 3]

	Example 5	Example 1	Example 6	Example 4
Anode Active Material	Li metal	Li metal	Amorphous carbon	Amorphous carbon
Additive	Compound No. 1	Compound No. 1	Compound No. 1	Compound No. 1
Electrolyte solvent	EC/DEC	EC/DEC	PC/EC/DEC	PC/EC/DEC
Capacity retention ratio (%) at 100 cycle	90.2	87.6	-	-
Capacity retention ratio (%) at 300 cycle	-	-	90.6	88.1

(Example 7)

The electrolyte solution containing the additive of compound No.1, 1, 3-PS, and further vinylene carbonate (VC) was applied to the present example. An aluminum foil having a thickness of 20 μm was used as cathode current collector, and LiMn₂O₄ was used as cathode active material in the cathode. Amorphous carbon and vapor-deposited lithium metal having a thickness of 20 μm on copper foil of anode current collector having a thickness of 10 μm were used as anode active material in the anode. The mixed solvent (volume ratio: 20/20/60) of PC, EC and DEC was used as solvent of the electrolyte solution. LiPF₆ of 1 mol/L was dissolved in this solvent. The addition of the compound No. 1 of 0.5 weight% was added to the total electrolyte solution, as an additive. Next, 1,3-PS of 1 weight% and VC of 1 weight% were added in the electrolyte solution respectively, and the electrolyte solution of the present example was fabricated. The secondary battery was fabricated by laminating anode and cathode with the separator which consists of polyethylene therebetween.

15 [0067]

(Charge/discharge cycle test)

The measurement was performed as the method described in example 1. Table 4 shows the result obtained.

[0068]

20 It is confirmed that the battery of example 7 has the more improved capacity retention ratio after the cycle test with reference to that of example 5, that is, the cycle properties is improved by further adding VC in the electrolyte solution which contains the compound represented by the general formula (1) and sulfonate compound different from the compound represented by the general formula (1).

[0069]

[Table 4]

	Example 7	Example 6
Anode Active Material	Amorphous carbon	Amorphous carbon
Additive	Compound No. 1	Compound No. 1
Electrolyte solvent	PC/EC/DEC	EC/DEC
Sulfonate compound	1% 1,3-PS	1% 1,3-PS
VC derivative	1% VC	None
Capacity retention ratio (%) at 300 cycle	90.9	90.6

(Examples 8 to 10)

The battery was fabricated and evaluated as example 4 except that the concentration of compound No. 1 as the additive was changed. The cycle properties was investigated as example 4. Table 5 shows the result thereof.

It is confirmed that the effects appear in 0.1 to 5 weight% of concentration of the compound represented by the general formula (1), from table 5.

[0070]

10 [Table 5]

	Example 4	Example 8	Example 9	Example 10
Anode Active Material	Amorphous carbon	Amorphous carbon	Amorphous carbon	Amorphous carbon
Concentration of compound No.1	0.5	1.0	5	0.1
Electrolyte solvent	PC/EC/DEC	PC/EC/DEC	PC/EC/DEC	PC/EC/DEC
Capacity retention ratio (%) at 300 cycle	88.1	90.2	89.1	86.1

(Example 11)

In the present example, the battery as example 7 was fabricated and the experiment was performed except that the compound No.3 was used as the additive represented by the general formula (1) and the complex oxide ($\text{LiNi}_{0.5}\text{Mn}_{1.35}\text{Ti}_{0.15}\text{O}_4$) which can obtain voltage of

15 4.5V or more was used as the cathode active material.

[0071]

It is confirmed that the battery of example 11 has the more improved capacity retention ratio after the cycle test with reference to that of comparative example 4, that is, if the complex oxide ($\text{LiNi}_{0.5}\text{Mn}_{1.35}\text{Ti}_{0.15}\text{O}_4$) which can obtain voltage of 4.5V or more was used as the cathode active material, the cycle properties was improved by using the electrolyte solution containing compound represented by the general formula (1). As a result of performing peak division of the sulfur spectrum by XPS analysis of the cathode surface, it was confirmed that the substance having a peak near 164 eV existed. Since such substance was not confirmed in the comparative example 4 with no compound No.3, it is conceivable that the membrane peculiar to the disulfonate compound of the present invention had been formed on the cathode.

10 [0072]

(Comparative Example 4)

The measurement as example 11 was performed except that the additive of the compound No.3 was not added in example 11. Table 6 shows the result of example 11 and comparative example 4.

15 [0073]

[Table 76]

	Example 11	Comparative Example 4
Anode Active Material	Amorphous carbon	Amorphous carbon
Additive of compound No.1	Compound No. 3	None
Electrolyte solvent	PC/EC/DEC	PC/EC/DEC
Capacity retention ratio (%) at 300 cycle	85.3	45.6

[BRIEF DESCRIPTION OF THE DRAWINGS]

[0074]

20 [FIGURE 1] FIG. 1 illustrates an outlined structure of one exemplary of a secondary battery according to the present invention.

[EXPLANATION OF REFERENCE]

[0075]

11 Cathode current collector

12 Layer comprising cathode active material

- 13 Layer comprising anode active material
- 14 Anode current collector
- 15 Non-aqueous electrolyte solution
- 16 Porous separator

[Document Name] ABSTRACT

[Abstract]

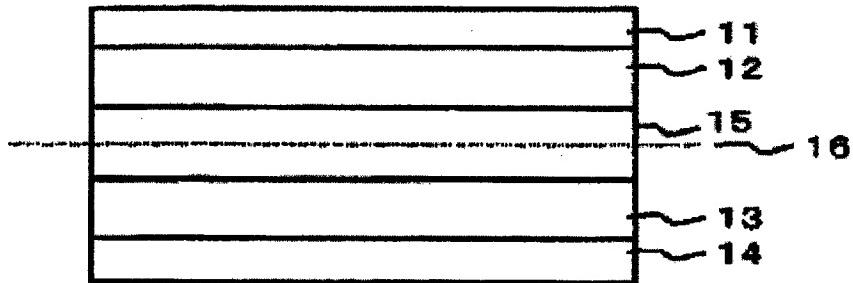
[Technical Problem] To obtain a secondary battery which has characteristic such as excellent energy density and electromotance and has excellent cycle life and safety

- 5 [Technical Solution] An electrolyte solution for secondary battery comprising a disulfonic acid compound in an aprotic solvent, or an electrolyte solution for secondary battery further comprising sulfonate compound or vinylene carbonate in this electrolyte solution is used.

[Chosen Drawing] FIG. 1

[Document Name] DRAWINGS

[FIG. 1]

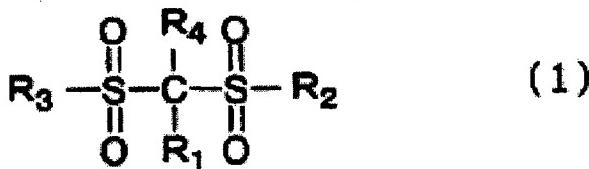


[Document Name] Claims

[Claim 1]

An electrolyte solution for secondary battery comprising an aprotic solvent and at least a compound represented by the following general formula (1):

5 [formula 1]



wherein R₁ and R₄ independently represent a hydrogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted alkoxy group, or a halogen atom; and R₂ and R₃ independently represent a substituted or unsubstituted alkyl group, a substituted or 10 unsubstituted phenoxy group, a substituted or unsubstituted alkoxy group, a hydroxyl group, a halogen atom, or a substituted or unsubstituted amino group.

[Claim 2]

The electrolyte solution for secondary battery according to claim 1, wherein the 15 electrolyte solution for secondary battery further comprises a lithium salt as an electrolyte salt.

[Claim 3]

The electrolyte solution for secondary battery according to claim 1 or 2, wherein the electrolyte solution for secondary battery further comprises at least one selected from the group 20 consisting of 1,3-propane sultone, 1,4-butane sultone, sulfolane, alkane sulfonic anhydride, cyclic disulfonate compound, γ -sultone compound and sulfolene compound.

[Claim 4]

The electrolyte solution for secondary battery according to any one of claims 1 to 3, 25 wherein the electrolyte solution for secondary battery further comprises at least one of vinylene carbonate and the derivatives thereof.

[Claim 5]

The electrolyte solution for secondary battery according to any one of claims 1 to 3, 30 wherein the aprotic solvent is at least one organic solvent selected from the group consisting of cyclic carbonates, linear carbonates, aliphatic carboxylates, γ -lactones, cyclic ethers, linear

ethers and fluoride derivatives thereof.

[Claim 6]

The electrolyte solution for secondary battery according to any one of claims 2 to 5,
5 wherein the lithium salt is at least one lithium salt selected from the group consisting of LiPF₆,
LiBF₄, LiAsF₆, LiSbF₆, LiClO₄, LiAlCl₄, LiN(C_kF_{2k+1}SO₂)₂ and LiN(C_kF_{2k+1}SO₂)(C_mF_{2m+1}SO₂),
wherein k and m are independently 1 or 2.

[Claim 7]

10 A secondary battery having a cathode, an anode and an electrolyte solution for
secondary battery characterized in that the electrolyte solution for secondary battery is the
electrolyte solution for secondary battery according to any one of claims 1 to 6.

[Claim 8]

15 The secondary battery according to claim 7, wherein the cathode includes a
lithium-containing complex oxide which can occlude and release lithium.

[Claim 9]

20 The secondary battery according to claim 7 or 8, wherein the anode includes a metal
material which can form an alloy with lithium metal or lithium as a anode active material
which can occlude and release lithium.

[Claim 10]

25 The secondary battery according to any one of claims 7 to 9, wherein the anode
includes carbon as an anode active material.

[Claim 11]

The secondary battery according to claim 10, wherein the carbon is graphite.

30 [Claim 12]

The secondary battery according to claim 10, wherein the carbon is amorphous carbon.